Japan Geoscience Union Meeting 2014
(28 April - 02 May 2014 at Pacifico YOKOHAMA, Kanagawa, Japan)

BAO01-P01 Room:Poster Time:April 28 18:15-19:30

Theoretical investigation of amino acid formations on interstellar dusts

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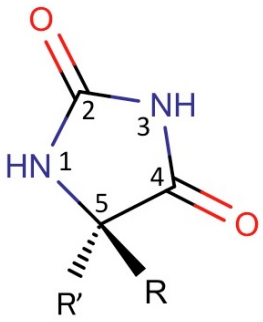
Molecular evolution in the interstellar space remains unsolved. Formations of molecules in space have been extensively studied by experiments and space observations. Formations of complex organic molecules are expected in the interstellar space. In fact, some amino acids were found in meteorites and amino acids were detected after UV irradiation of interstellar ice analogs.

In the amino acid formation in space, many precursors and molecular evolution pathways are expected. Among these possible pathways, it is very important to know the energy profiles and molecular structures in the major formation pathways. In this study, possible amino acid formation pathways are investigated by using accurate quantum chemistry methods at the density functional theory levels.

Two formation pathways of glycine and alanine were examined: (1) hydrolysis of aminoacetonitrile and (2) hydrolysis of hydantoin derivatives. In the aqueous solution model, Polarizable Continuum Model was used.

Calculated formation energy of glycine is the most stable in the formation pathway in vacuum and no excessively stable intermediates existed. In aqueous solution, hydantoin pathway was slightly unstabilized. In conclusion, glycine production is considered to be occured easily if the components exist. Similar trend is expected for the alanine production.



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BAO01-P02 Room:Poster Time:April 28 18:15-19:30

Cosmic dusts capture on the International Space Station: Progress of the ground-based experiment

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Introduction: Organic matter in interplanetary dust particles (IDPs) records the primitive chemical history in the early Solar System as well as it is thought to have delivered the building blocks of life to the early Earth (Chyba and Sagan, 1992). The Japanese Astrobiology working group, Tanpopo, is planning to collect the IDPs using a low-density silica aerogel (0.01 g/cm^3) (Tabata et al. 2011) on the International Space Station (Yamagishi et al. 2009). The mission has a great advantage that collection of the pristine IDPs without atmospheric entry heating and terrestrial contamination will be expected. One thing that has to be considered is a possible modification of the chemical composition of organic matter in IDPs upon their high velocity impact to the aerogel. This issue has been also concerned in the Stardust cometary dust sample return mission. Although the laboratory simulations have been conducted to study the alteration of minerals (Okudaira et al. 2004; Noguchi et al. 2007), the alteration of organics under a realistic condition has not been well understood. As a ground-based experiment, we have conducted a laboratory experiment of aerogel capture of Murchison meteorite powder at 4 km/s using a two-stage light gas gun, in order to evaluate the extent of modification of organic matter in the meteorite.

Experimental: The Murchison meteorite powder (˜500 ug) of a particle diameter of 30-100 um in a polycarbonate sabot was shot at ˜4 km/s using a two-stage light gas gun at JAXA/ISAS. The penetrations of the meteorite powder formed ˜70 tracks of ˜10 mm length in aerogel. Six terminal particles were extracted from the aerogel tracks using a tungsten needle and were pressed between two Al foils. The particles on the Al foils were analyzed by micro-Fourier transmission infrared (FTIR) spectroscopy at the beamline 43IR, Spring-8 and Osaka Univ., and micro-Raman spectroscopy at Osaka Univ. For a comparison, pre-shot Murchison meteorite powder was analyzed by these micro-spectrometers.

Results and discussion: The IR imaging detected the regions of absorptions of aliphatic carbons, CH3 at 2960cm^{-1} and CH2 at 2920cm^{-1} within the two Murchison terminal particles captured by aerogel. Thus, organic matter is survived through the high velocity impact at 4 km/s. The spectral intensities of aliphatic carbons in the terminal particles are slightly lower than those in the pre-shot Murchison meteorite. CH2/CH3 ratios obtained from the IR spectra of the terminal particles were 0.3 ? 3, while those of the pre-shot sample were 1.3 ? 2. The difference in the ratios may be reflected by modification of aliphatic chains of organic macromolecules in the meteorite, e.g., demethylation, methylation, or cracking, due to the high velocity impact heating. From the two terminal particles, D- and G- bands, which are derived from carbonaceous matter, were detected by micro-Raman analyses. Peak widths and positions of the two bands showed similar values to those for pre-shot Murchison meteorite. Thus, modification of aromatic structures after the aerogel capture is unlikely. Although relative amounts of organics were low in the four other terminal particles, this may be reflected by original heterogeneity of the meteorite.

Keywords: International Space Station, Cosmic dusts, Organic matter, Astrobiology, Origin of life, Aerogel

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BAO01-P03 Room:Poster Time:April 28 18:15-19:30

Possibility of production of amino acids by impact reaction using a light-gas gun as a simulation of asteroid impacts

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We are interested in the production process of amino acids in space. Especially, asteroids coming to Titan satellite have made impact reaction on the surface including nitrogen gas, water ice and methane. On the Titan surface, various material, produced by the impact reactions, have been stored under low temperature and dark condition. To do the simulation experiment, a JAXA 2-stage light-gas gun has been used. A projectile with 6.5km/s of speed hits a water + iron target in 1 atm of nitrogen gas, causing an impact reaction. Figure 1 shows a crater on the target. Figure 2 shows produced black soot which deposited onto the aluminum sheet. The samples produced are carefully collected and analyzed by HPLC, FTIR, TOF-MS. As a result of HPLC, peaks suggesting the existence of glycine and alanine in the samples produced were confirmed.

Keywords: impact reaction, gas gun, Titan, asteroid, amino acid, HPLC

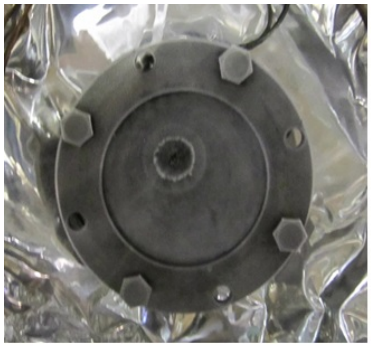

Fig.1 A crater on the target.

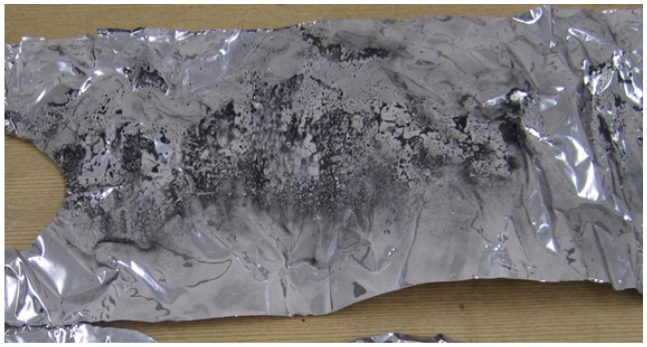

Fig.2 Produced black soot deposited onto the aluminum sheet.

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BAO01-P04 Room:Poster Time:April 28 18:15-19:30

Amino acid formation from simulaed mildly-reducing primitive atmospheres by spark discharges and proton irradiation

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Miller (1953) reported that amino acids were abiotically formed in a gas mixture of methane, ammonia, hydrogen and water. However, It is suggested that the primitive Earth atmosphere was less reducing, and its major components were carbon dioxide and nitrogen. It is quite difficult to form amino acids from such non-reducing gas mixtures. If it is mildly reducing, i.e. it contained some carbon monoxide or methane, amino acid production could be expected.

We examined possible formation of amino acids from mildly reducing gas mixtures by spark discharges or by proton irradiation. A mixture of carbon dioxide and methane (total 50 %) and nitrogen (50 %) was introduced into a glass tube with liquid water. Spark discharges in the gas mixtures were performed with a Tesla coil for 12 hours. Proton beams (2.5 MeV, 2 mC) were irradiated to the gas mixtures from a Tandem accelerator (TIT). The resulting products were acid-hydrolyzed, and amino acids were determined by ion-exchange HPLC with post-derivatization with o-phthalaldehyde and N-acetyl-L-cystein.

A mixture of methane and nitrogen gave amino acids in high yields by either spark discharges or proton irradiation. When carbon dioxide was added to the gas mixture, amino acid yields decreased. In the case of spark discharges, amino acids could not be detected when methane ratio in total carbon sources (carbon dioxide + methane) was less than 30 %. In the case of proton irradiation, the mixture with the methane ratio was 5 % still gave amino acids. Thus, it was suggested that, in the case that the primitive Earth atmosphere was only slightly reducing, a major energy source for the production of amino acids was not thundering but cosmic rays.

Keywords: mildly-reducing primitive atmospheres, spark discharge, proton irradiation, origins of life, amino acids

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BAO01-P05 Room:Poster Time:April 28 18:15-19:30

Stability and reactions of amino acids in simulated submarine hydrothermal systems

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The discovery of hydrothermal systems in the late 70s brought a new hypothesis to the origin of life. Previously, the Urey-Miller experiment had made waves in this new field, indicating that a reducing atmosphere could form amino acids from basic chemicals. The further discovery of hydrothermal systems with earth prebiotic conditions added another notion to the field. Since then, different kinds of simulation were conducted to test the hypothesis. Initially and autoclave was extensively used due to its robustness and durability, however this system was not an ideal system, hence a flow-type simulator was proposed instead. We tested the stability and reaction of several amino acids using a flow reactor simulating submarine hydrothermal systems at 200 — 250 ℃. This study generally showed that there is a variation in the individual amino acids survivability in the simulators. This is mainly attributed to the following factors; heat time, cold quenching exposure, metal ions and also silica.We observed that, in a rapid heating flow reactor, high aggregation and/or condensation of amino acids could occur even during a heat exposure of 2 min. We also monitored their stability in a reflow-type of simulator for 120 min at 20 min intervals. The non-hydrolyzed and hydrolyzed samples for this system showed a similar degradation only in the absence of metal ions. We also tested the possible condensation that could be forming peptide bonds among the amino acids in one of the flow rectors. We utilized the Lowry protocol to determine the concentration of the peptide bonds in several hydrothermal temperatures. Concentration of peptide bonds was significantly higher when the temperature was at 300 ℃. This is despite the decomposition of amino acids by more than half. However, the contribution of peptide bonds in the combined amino acids was less than 10%, even in the 300 ℃ sample, which showed the highest contribution of peptides. The major heat products were non-peptide amino acid condensates (NPACs) that only possess partial peptide bonds. The role of NAPCs should be examined though they were often ignored in the classical chemical evolution scenario so far.

We experimented with Gly, Ala, Asp and Val in the SCWFR at 200 ℃, 250 ℃ and 300 ℃. We recorded the recovery of the samples and performed the Lowry method to quantify the peptide bond concentration. Peptide bonds ' concentrations are significantly higher when the temperature is at 300 ℃. This is despite the decomposition of amino acids by more than half. The highest peptide bond concentration among the samples constitute only about 10% of the total product yield of the amino acid mixture.

We also examined possible formation of amino acid condensates by using single amino acid (Gly, Ala, Asp or Val) and compared the results with those with all of four amino acids.

Keywords: submarine hydrothermal systems, amino acids, origins of life, flow reactor

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Scanning electron microscopic observation of organic microspherules formed by Maillard-type reaction

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It has been suggested that organic microspherules played a role as a physical container to maintain catalytic molecules and their reaction intermediates at concentrations high enough to sustain catalysis in prebiotic chemistry on the early Earth (Weber, 2005). Experimental studies on the formation of organic microspherules from a variety of organic compounds, such as amino acids (Fox and Harada, 1958), gelatin and gum arabic (Oparin, 1976), organic extracts from meteorite (Deamer, 1985; Deamer and Pashley, 1989), interstellar organic analogue (Dworkin et al. 2001), fatty acids and polycyclic aromatic hydrocarbons (Groen et al. 2012), formaldehyde and ammonia (Cody et al. 2009; Kebukawa et al. 2013) have been reported. However, the formation process and stability of these organic microspherules have been unexplored. In this study, sizes, shapes, and distributions of organic microspherules formed during the progress of Maillard-type reaction of formaldehyde and ammonia were investigated.

Experimental:
Paraformaldehyde (120mg), glycolaldehyde (120mg), ammonium hydroxide (54ul), calcium hydroxide (30mg) in 2ml of water in a glass tube was heated at 50-90 degrees C for 71-720 hours. For comparison, the samples without ammonium hydroxide were heated under the same conditions. After heating, the sample solutions were centrifuged. The precipitated material were rinsed with 2N HCl to dissolve calcium, and dried at 50 degrees C to obtain organic solids. The organic solid samples were pressed on a indium plate, gold-coated, and observed by a scanning electron microscopy (SEM).

Results and discussion:
After several minutes in heating, all the sample solutions turned yellow and eventually turned brown to black. Organic solids were produced at 90 degrees C but 50 degrees C. The yields of organic solids from sample solutions with ammonia were 10 times higher than those without ammonia. The yields gradually increased during heating. While distorted-shaped aggregates are produced from the samples heated for 71-120 hours, micron-sized organic microspherules (0.4-4.0 um) were observed from those heated for 240-720 hours. The samples with ammonia show perfectly round shapes of microspherules. Some microspherules are large and oval in the sample heated for 480 hours. The sizes of the microspherules increased with heating time. Organic solids produced by the same reaction as this study's at 90 degrees C for 72 hours consist of approximately equal abundances of aromatic and aliphatic carbons (Kebukawa et al. 2013). This molecular composition could result in amphiphilicity that is related to formation of the stable microspherules observed in this study. Formaldehyde and ammonia are thought to have been commonly present on the early Earth, and thus the organic microspherules formed by these molecules which proceed polymerization efficiently under mild conditions, could have played a role as a precursor of prebiotic cell membrane.

Keywords: organic microspherules, Maillard reaction, prebiotic cell membrane

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BAO01-P07 Room:Poster Time:April 28 18:15-19:30

Fluorescence imaging of microbe-containing micro-particles that had been shot from a two-stage light-gas gun into an ult

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We previously proposed an experiment (the Tanpopo mission) to capture microbes and organic compounds on the Japan Experimental Module of the International Space Station. An ultra low-density silica aerogel will be exposed to space for one year. After retrieving the aerogel, particle tracks and particles found in it will be visualized by fluorescence microscopy after staining it with a DNA-specific fluorescence dye. In preparation for this study, we simulated particle trapping in the aerogel so that methods could be developed to visualize the particles and their tracks. During the Tanpopo mission, particles that have an orbital velocity of about 8 km/s are expected to collide with the aerogel. To simulate these collisions, we shot *Deinococcus radiodurans*-containing Lucentite particles into an aerogel from a two-stage light-gas gun (acceleration 4.2 km/s). The shapes of the captured particles and their tracks and entrance holes were recorded with a microscope/camera system for further analysis. The size distribution of the captured particles was smaller than the original distribution, suggesting that the particles had fragmented. We were able to distinguish between microbial DNA and inorganic compounds after staining the aerogel with the DNA-specific fluorescence dye SYBR green I as the fluorescence of the stained DNA and the autofluorescence of the inorganic particles decay at different rates. The developed methods are suitable to determine if microbes exist at the International Space Station altitude.
Keywords: Aerogel, Space experiment, Hypervelocity impact experiment, DNA-specific fluorescence dye.

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Studies on life detection methods by using enzymatic activities: Phosphatase and Catalase

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We have recognized that microorganisms can survive in such extreme environments as polar environments, deserts, hot springs and stratosphere. It is quite difficult to evaluate microbial activities in extreme environments, since most microorganisms in extreme environments are hard to cultivate. We are discussing how to detect microorganisms in extreme environments including Mars. In MELOS mission, a proposed Japanese Mars exploration, fluorescence microscope will be applied to life detection. In addition to the technique, we examined amino acid analysis and enzyme assay as possible chemical strategies for life detection in terrestrial and extraterrestrial extreme environment.

One of the most well studied enzymes in environments is phosphatase. Phosphatases hydrolyze phosphate esters to produce phosphate that is essential for terrestrial life, and they are known to be stable in environments. We assayed rocks and soils in extreme environments such as submarine hydrothermal core samples and Antarctic soil samples, and found that it can be a good indicator for microbial activity. Here we analyzed phosphatese activity in Atacama Desert soil samples. Atacama desert is know to be one of the driest and harshest environments on the Earth, and regarded as Mars simulant. Samples were collected in 2002 by USA-Mexico team. Phosphatase activity was correlated to precipitation rate.

Such extreme environments as Mars, Antarctica and deserts have commonalities. Strong UV causes formation of peroxides that will damage bioorganics. Thus, we supposed that catalase and peroxidase are quite important for the survival of organisms living there, and it would be a good biomarker. We are now studying the assay methods for catalase in soil samples.

Keywords: extreme environments, Mars, life detection, enzymatic activities, phosphatase, catalase

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Molecular approach to the characterisation of Sri Lanka red rain cells

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The recent mysterious phenomenon that has attracted much attention is that of the red rain which fell in Polonnaruwa, Sri Lanka, on 13 November 2012. The microbial content in red rain shows generic similarities to that of the Indian red rain which fell in 2001. The morphological property of those microbes has been well documented [1,2]. Various microscopic analyses of our Sri Lankan red rain sample indicate that the defining red rain cells (RRC) exist in the presence of other microorganisms including diatoms. In our past paper, the ultrastructure of RRC shows that it is possibly a spore-form and so allowing them to thrive in the extreme upper biosphere conditions [3]. We also show the presence of uranium in the abnormally thick cell wall of RRCs.

In this report, we present the molecular approach to the characterisation of microbial communities in red rain and reveal the genus of RRCs. A beads-beating protocol is carried out for the efficient extraction of DNA and denaturing gradient gel electrophoresis (DGGE) for the analysis of microbial communities.

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Keywords: Red rain, Extremophile, Polonnaruwa

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BAO01-P10 Room:Poster Time:April 28 18:15-19:30

The mechanism that had formed the oldest organic carbon with the banded ironstone formations

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The band iron layers were formed about 3.8 billion years ago. M. T. Rosing reported that the oldest organic carbon was found in the sedimentary rock from west Greenland that formed at the same period [1]. That is, the value of carbon isotope ratio ($^{12}C/^{13}C$) on 2- to 5-micrometers graphite globules in the rock is larger than that of inorganic carbon. Since photosynthesis is realized by a system of molecules with chain of reactions, the production of that carbon by the photosythesis is difficult. The author proposes the mechanism that a slightly large amount of ^{12}C was incorporated in the floating substances which were produced with the banded ironstone formations (BIF).

We can observe the phenomena by adding fine iron particles in carbonated water as shown in the [photograph 1]. Bubbles were produced at the surface of iron in the bottom of water. The bubbles transfer the fine particles of iron from the bottom to the surface. Since the electronegativity of carbon is larger than that of hydrogen, the carbon atom released from carbonated water by oxidation of iron was adhered to iron particle. The intermolecular bonding of iron with carbon beomes floating substance. The iron atom will be released from the floating substance as the form of iron oxide. So, the carbon atom that was released from the iron will constitute the floating substances [2].

At about 3.8 billions years ago, earth's surface was covered with compounds such as oxides, sulfides and carbonates. Although there were carbon dioxide gasses in the atmosphere, the seawater at mild temperature became dissolve the carbon dioxide. There occurred volcanic eruptions frequently. Iron particles were emitted by the volcanic eruption and the iron oxides were deposited at the bottom on the sea. that is the process of BIF. On the other hand, the carbn dioxide molecules in the syk smashed into surface of the sea water frequently. It is possible to produce an organization of molecules from the floating substance of intermolecular bonds by the energy that comes from outer world such as ultraviolet ray. The floating substances will accuulate at surface of water. At last, the substances deposited at bottom of the sea. That is, the carbon atoms those were included in sedmentary rocks fromk west Greenland had come from the sky.

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[**Photograph 1**]

Accumulation of the floating substances those are produced by adding fine iron particles in carbonated water (Left: old #300 meshed fine particles, Center: new #300meshed fine particles, right: #200 meshed particles)

Keywords: 3.8 billion years ago, Banded iron formation, Organic carbon, Carbon dioxide, Carbon isotope ratio